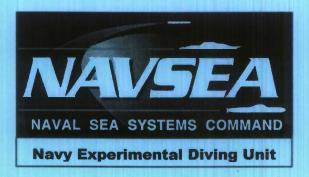
Navy Experimental Diving Unit 321 Bullfinch Rd. Panama City, FL 32407-7015

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A REVIEW OF CURRENT AIR SCREENING PROCEDURES FOR BALLAST TANK DIVING



Authors:

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19. ABSTRACT

During underwater ship husbandry operations on submarines, divers enter the main ballast tanks to repair or modify electrical or mechanical systems. Before the divers are permitted to remove their diving equipment to increase their mobility, efficiency, and comfort during their work, gas free procedures are currently used to confirm the chemical safety of ballast tank atmospheres at pressures up to 2 atmospheres absolute (ATA). During multiple visits to two different shore sites where ballast tank diving was occurring, we reviewed these air screening methods and collected air samples from ballast tanks as a first step toward developing a uniform set of procedures to improve the ability to ensure safe, breathable air during ballast tank diving. The gas free procedures used at the two commands that we visited were similar but failed to screen for volatile organic compounds (VOCs), did not always test for CO₂, and were not always performed at hourly intervals during the diving operation. In view of the elevated levels of VOCs and CO₂ found in some of our samples. these screening failures put diver safety at risk. In our opinion, instead of gas free screening (with its ambiguity about what gases should be monitored), the emphasis of any air testing should be on ensuring a safe, breathable atmosphere inside the ballast tank during diving. Consequently, upon entry into ballast tanks, before diving equipment is removed, the ballast tank atmosphere should be evaluated for its chemical safety in terms of O₂, CO₂, CO, and VOCs. The current approach of using the Occupational Safety and Health Administration (OSHA) guidance to set limits for CO₂ and CO appears reasonable, although a mechanism should be established to update U.S. Navy procedures when OSHA makes a substantial change in exposure limits. However, we recommend that the current OSHA exposure limits for CO₂ and CO should be divided by a factor of 2 to correct for the maximum depth (2 ATA) to which ballast tank dives are conducted, a correction reflecting the twofold increase in partial pressure of contaminants to which divers could be exposed. Following this review, the next step will be to develop revised air screening procedures for ballast tank atmospheres, procedures based on our recommendations about setting a VOC limit and selecting a screening instrument.

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INTRODUCTION

During underwater ship husbandry operations on submarines, divers enter the main ballast tanks (MBTs) to repair or modify electrical or mechanical systems. These diving operations most commonly occur while submarines are in port on the surface and the ballast tanks are filled with air. During these operations, divers are required to use a surface-supplied air system¹ that can be cumbersome when they are working in such confined spaces. Consequently, after the atmosphere of the ballast tank has been flushed with an air volume estimated to be two times that of the gas space and confirmed to be safe by testing, divers are permitted to remove their diving equipment to increase their mobility, efficiency, and comfort during their work.¹

The current requirement is for the ballast tank atmosphere to be checked by using gas free procedures before breathing apparatus are removed and then rechecked every hour thereafter during the diving operation. However, the reliability of these procedures to ensure safe, breathable air during ballast tank diving is unknown due to questions about (1) the nature of contaminants in ballast tank atmospheres, (2) the effectiveness of the procedures to screen the air for contaminants of concern, and (3) the safe exposure limits for these contaminants in closed spaces at pressure. Another concern is that the gas free procedures described by Naval Sea Systems Command (NAVSEA) do not specify what substances should be monitored or which instruments used for a given situation, and thus, such procedures may differ from command to command. ^{2,3}

Although we are aware of few problems that have occurred during ballast tank entries due to air contamination, the Navy's current emphasis is on minimizing long-term effects of exposure to contaminants and other hazards, an emphasis evidenced by the recent establishment of the Submarine Atmosphere Health Assessment Program as well as other safety programs. Consequently, the Navy is interested in developing a uniform set of procedures to improve the ability to ensure safe, breathable air during ballast tank diving. This report describes the initial step taken to develop such procedures — that of reviewing current screening methods, including a contaminant survey of ballast tank atmospheres. These results will allow us to define what contaminants, and at what levels, should be monitored in ballast tanks. Our work is limited to ballast tank diving associated with SSN 688 class submarines.

BALLAST TANK AIR QUALITY CONCERNS

Volatile contaminants in the gas space of any ballast tank should originate primarily from the air supply to the ballast tank and the ballast tanks themselves. Except for CO₂ and a few other metabolic gases, no significant contamination is expected from the divers — unless they make a contaminated water entry or bring with them equipment and tools that offgas residual solvents or other volatile contaminants.

The low pressure main ballast tank (LP MBT) blow system is used to expel water from the MBTs of SSN 688 class submarines.⁴ As part of this process, the snorkel induction

system draws fresh air into the ship's fan room, where the LP MBT blow system takes its suction. While submarines are at the surface and in port, the LP MBT blow system is used when needed to remove any water that has subsequently entered the ballast tanks due to air leakage and to ventilate the air-filled ballast tanks as required for diver operations. For a view of the locations of the MBTs on an SSN 688 submarine, see Figure 1.

When submarines are in port, the outside air can potentially be contaminated by port activities such as cleaning and painting as well as by the exhaust from any internal combustion engines operating in the area. Outside air, when delivered to the fan room by the snorkel induction system, will then mix to some degree with the submarine atmosphere before it enters the intake of the LP blower. Whether this mixing introduces significant amounts of volatile contaminants from the submarine atmosphere into the air delivered to the ballast tanks depends partly on how well the submarine has been ventilated before the LP MBT blow system has started up. Fortunately, the large majority of atmospheric contaminants commonly found on submarines are often present in only very low amounts, and normally they present no toxic hazard. However, the pressure inside a ballast tank during diver entry may reach approximately two atmospheres absolute (ATA) for SSN 688 class submarines. Thus, in comparison to exposures at one ATA, exposures in the ballast tank subject divers to up to a twofold increase in partial pressure of any contaminants.

Based in part on past research with other closed-space environments, the potential for the ballast tank to contribute to the contaminant load of its atmosphere must also be considered. In the case of sonar domes on U.S. Navy surface ships where human entries are also periodically made, significant levels of contaminants inside the domes have been attributed to the offgassing of the domes themselves.⁵ For ballast tanks, the hardware and wiring (including the sonar arrays) contained within might also be expected to generate volatile contaminants, as would any recent painting of the inside of the ballast tanks. In addition, marine growth inside the ballast tank may produce atmospheric contamination. Lastly, whether diver-expired CO₂ causes significant increases in the CO₂ of the ballast tank atmosphere during an operation is unknown.

METHODS

REVIEW EXISTING PROCEDURES

The existing procedures used in the Fleet were examined to determine what contaminants are being monitored now and how reliable the screening appeared for these chemicals. This review was performed by visiting shore sites where ballast tank diving was occurring to observe procedures and discuss issues with Fleet personnel. We hoped to answer some, if not all, of the following questions:

- (1) Are the same air screening procedures used everywhere by everyone involved with the testing?
- (2) What chemical species in the ballast tank atmosphere are being monitored (i.e., what are the "target species"?) and at what levels?
- (3) What is the condition of the air analyzers being used, and are maintenance, calibration, and operating procedures for the analyzers adequate to ensure reliable measurements?
- (4) Is the ballast tank atmosphere sampled in a way to allow accurate measurements of all target species?
- (5) How are the gas screening results used to decide whether the ballast tank atmosphere is safe, and what happens if the atmosphere is declared unsafe?

CONTAMINANT SURVEY

Concurrent with the on-site review of existing procedures, air samples were collected from the ballast tank atmospheres of a limited number of SSN 688 class submarines to determine the contaminant profile of ballast tank air. One important question was whether any contaminants that were not currently being monitored were of concern and therefore should be added to the target species list. Our goal was to sample the air from the ballast tanks of at least five different submarines with high-purity evacuated 500 ml stainless steel gas collection cylinders suitable for storing parts per million (ppm) levels of a range of volatile organic compounds (VOCs) for at least several months.

The sample cylinders were carried down to the ballast tanks by the working divers participating in our study. Before use, cylinders were loaded into a heavy-duty nylon bag that was then placed into a waterproof bag sold as a liner for the "Alice" rucksack by Diving Unlimited International, Inc. (San Diego, CA). The waterproof bag was placed into a mesh bag for protection before being carried down to the ballast tank, where the cylinders were removed from the bags and used to take samples at various locations inside the tank.

Within each ballast tank, triplicate samples were normally taken at each of four locations: forward upper, forward lower, aft upper, and aft lower — all positions relative to the submarine. Where insufficient cylinders were available for complete sampling, fewer than four locations within the ballast tank were sampled. Divers took samples by first moving to the sample location, slowly opening one of the two valves on each cylinder, and then allowing ~30 seconds for the cylinder to equilibrate with the ballast tank pressure before closing the valve. All divers had been instructed to hold each cylinder away from their bodies and to avoid breathing close to the cylinder during sampling. As samples were being taken, the divers relayed sampling information (e.g., cylinder number and location) to topside personnel who recorded that data and time. After sampling was completed, all cylinders were repacked in the bags and transported to the surface and onto the dive boat, where they were removed from the bags and dried before being repacked for final transport to NEDU.

Our gas analysis laboratory at NEDU subsequently analyzed samples to characterize the contaminant profiles. Gas chromatography (GC) was used to analyze samples — with a thermal conductivity detector for O₂ and with a methanizer/flame ionization detector (FID) for CO₂ and CO. Primary gravimetric standards with concentrations close to observed values were used to quantify these GC results.

Gas chromatography with FID and with mass spectrometry (MS), as described in Lillo and Caldwell, was also used to analyze samples for a broad range of VOCs. GC/FID was used, when it was possible, to identify organic species by comparing GC retention times of sample peaks to those times of the species in commercially acquired primary gas standards. One standard contained Freon 113, methyl chloroform, benzene, toluene, and xylenes, each ~10 ppm in air. A second standard contained methane, ethane, propane, butane, pentane, and hexane, again each ~10 ppm in air. A third standard contained a mixture of common freons: Freon 11, 12, 22, 113, and 114, each ~10 ppm in air. For GC/MS, a standard similar to the first 10 ppm mixture was used, except that each component was ~2 ppm. Our experience that many of these chemicals have been found in diving gases and diving facilities provided the basis for our choice of these gas standards. We identified contaminants by GC/MS by carefully reviewing library search results obtained from the NIST/EPA/NIH Mass Spectral Database (NIST107) with Shimadzu CLASS-5000 software.

Quantification of organic contaminants was based on the VOC gas standards and the GC/FID or GC/MS peak areas. Individual contaminants other than the chemicals in the gas standards were quantified in relation to the species in the standard closest to their retention times.

RESULTS AND DISCUSSION

From March 2002 to April 2003 we made a total of five visits (see Table 1) to two different ballast tank diving sites: Shore Intermediate Maintenance Activity (SIMA), Norfolk, VA, and Submarine Base, San Diego, CA. Our visits allowed us to observe ballast tank diving operations, to review gas free procedures, to discuss relevant issues, and to collect samples from the ballast tanks of five different SSN 688 class submarines. We visited and took samples twice from two of these five submarines on two different trips; from the remaining three submarines that we visited, we collected samples only once. A sixth submarine (USS ALBANY) was not visited but was sampled by the personnel conducting the diving operation.

REVIEW EXISTING PROCEDURES

We were told during some visits that the LP blow to ventilate the ballast tanks had been performed either the evening before or the morning of the dives. However, we had no way to verify whether the ventilation requirement always had been met either during our

trips or during all ballast tank operations. An officer on one submarine told us that he had assumed that the requirement to flush the ballast tank with twice its estimated volume was satisfied by completing a 5–10 min LP blow every morning to "top off" the ballast tanks. We were also told that the daily ventilation maintained the ballast tank entry of SSN 688 class submarines at a water depth of 27 feet of seawater (fsw) or ~2 ATA.

During our visits, the diving personnel always arranged to have a person who was qualified to perform gas free procedures check the ballast tank atmosphere at the start of operations so that divers could remove their gear while they were inside the tank. However, we observed several times that satisfying the gas freeing requirement delayed the start of diving by up to several hours because a gas free engineer was unavailable at the time requested by the divers. The diving personnel at SIMA, Norfolk, told us that they had tried to avoid these delays by qualifying some of their divers as gas free engineers who could then conduct the gas screening themselves. The divers at the Submarine Base, San Diego, relied on SIMA, San Diego, to supply their gas free engineers.

The gas screening procedures observed at the two commands we visited were similar and involved measuring O₂, CO₂, CO, combustible gas, and H₂S, but CO₂ was not always monitored. The ballast tank air was sampled topside on the dive boat by using either the pneumo hose on the diving umbilical line or a length of Tygon tubing. Before sampling the air, the divers took the hose or tubing into the gas space of the ballast tank and cleared it of any water by blowing pressurized diving air down through it from the boat. Forced upward by the higher-than-atmospheric pressure in the ballast tank, air from the ballast tank then began flowing back to the boat and was used to purge a small plastic bag (e.g., sandwich bag). At one command, gas measurements were taken as gas was flowing with the analyzer inside the bag; at the other command, measurements were taken with the analyzer inlet inserted into the bag's opening.

Air screening analyzers

The two instruments we observed at each site are listed below, although we were told that other instruments were also used to screen the air.

SIMA, Norfolk analyzers

- 1. Biosystems PhD Ultra (Biosystems, Inc.; Middletown, CT): O_2 , combustible gas, CO, H_2S . Alarm values noted during one visit included: low O_2 = 19.5% and high O_2 = 22.0%, 35 ppm CO, and 10 ppm H_2S . These values are the same as those of the default time-weighted average (TWA) alarm settings for this instrument. We are unsure of the combustible alarm value setting.
- 2. Bachrach CO₂ analyzer 2815 (Bachrach, Inc.; New Kensington, PA): CO₂.

Submarine Base, San Diego analyzers

- 1. GasTech GT-402 (GasTech, Ltd.; Osborne Park, WA): O₂, combustible gas, CO, and H₂S.
- 2. GasTech GT-CO₂ (GasTech, Ltd.; Osborne Park, WA): CO₂.

Exposure limits

Two gas free instructions (*Naval Ships' Technical Manual*² for forces afloat and *Gas Free Engineering Manual*³ for shore-based facilities) both define acceptable O₂ levels as 19.5–22.0% and acceptable combustible gas levels as less than 10% of the lower explosive limit (LEL). These two gas free instructions also define acceptable levels of toxic gases to be below the permissible exposure levels (PELs) set by the Occupational Safety and Health Administration (OSHA). These PELs are TWA concentrations that are set for the normal workplace and must not be exceeded during any eight-hour shift of a 40-hour work week.

The Naval Ships' Technical Manual² lists PELs for the three toxic gases monitored during ballast tank operations as 5000 ppm CO₂, 50 ppm CO, and 10 ppm H₂S. These values agree with the alarm values we observed at SIMA, Norfolk, for O₂ and H₂S but not for CO. These PELs for CO₂ and CO agree with 2005 OSHA values cited in the NIOSH Pocket Guide to Chemical Hazards;⁸ however, current OSHA guidance for H₂S gives no TWA value and a ceiling limit of 20 ppm, a limit which should not be exceeded during any part of the working time. As OSHA recommendations change with time, disagreement between gas free instructions written earlier and current limits is expected. However, it is unclear whether any mechanism is established to modify U.S. Navy exposure limits for ballast tank air if OSHA substantially changes one or more of the PELs.

Gas free testing results

We observed no cases where the gas free engineer found ballast tank air to exceed the gas free limits. Unfortunately, due to the multiple activities often occurring on the boat and the related crowded conditions in preparation for the dives, we were not always able to closely observe the gas free engineer when he sampled the air. We also did not observe any additional gas free testing being done, as required by the *Diving Manual*, on an hourly basis following the initial test.

The limited gas free data that we recorded revealed that all measurements for H_2S and combustible gas were 0 ppm and 0% LEL respectively. All observed measurements — except one, for CO — were 0 ppm. The one exception for CO was the 13 June 2002 sample from USS HAMPTON, where 7 ppm was measured by the gas free engineer. One other exception for CO of 3 ppm was also noted on the recorded data supplied to

us by the personnel from USS ALBANY, the one submarine that we did not personally visit.

We observed also that CO_2 was commonly not measured — due, we were told, to the unavailability of a working CO_2 analyzer. The gas free engineers' few CO_2 measurements that we recorded were no higher than 1500 ppm. We also observed times when the gas free instruments appeared to be malfunctioning (e.g., giving negative readings for combustible gas), but the air was always declared to be acceptable for diving.

Other observations and comments from the divers

We discussed many ballast tank issues with the on-site personnel during our visits to Norfolk and San Diego. This section presents a few of the more informative comments, although in many cases we have no ability to confirm how reliable they are or how well they represent the views of personnel at other diving sites.

- 1. One gas free engineer told us that the gas free course and gas free instructions did not address how gas freeing applied to the diving situation. For example, no depth correction exists for the gas free limits. This same engineer requested guidance and a set of procedures that better addressed possible contamination in the ballast tanks.
- 2. Several gas free engineers told us that some of the analyzers we saw used during gas screening were different from those taught in the gas free course. One gas free engineer also admitted that he did not always calibrate the analyzers and did not always know the calibration history of the analyzers he used.
- 3. We reviewed with one gas free engineer the calibration, maintenance, and repair procedures he used with his instruments; this discussion, held on shore in his instrument shop, allowed us to see a hands-on demonstration of many of these procedures. This review suggested that adequate procedures were probably established to ensure the reliability of gas measurements by this one engineer.
- 4. One veteran ballast tank diver said that he had never noticed a difference in odor inside ballast tanks between boats that had recently come into port and those that had been in port for a few weeks.
- 5. Personnel at the diving sites reported only rare incidents of high CO or CO₂ readings, low O₂ readings, and diver mishaps. No problems with H₂S or combustible gas were mentioned. One gas free engineer said that he remembered only one major incident that had occurred in his 15 years of experience: a diver had to be pulled from a ballast tank because of high CO. However, one veteran diver said that he sometimes had suffered bad headaches following a diving operation.

CONTAMINANT SURVEY

Gas analysis results for O_2 , CO_2 , and CO are presented in Table 2. Because the O_2 levels of samples taken at different locations within each ballast tank were similar (with two exceptions, varying over a range of $\leq 0.4\%$), the O_2 value for each ballast tank is reported as the average of the different samples. For O_2 , all samples met the 19.5–22.0% O_2 gas free requirement. However, the CO_2 level for each ballast tank varied substantially with sample location, presumably due to poor gas mixing within the ballast tank, and therefore is reported as the range of the different samples.

Uncorrected for pressure, all laboratory CO₂ samples were below the 5000 ppm gas free PEL but were generally two to three times higher than the gas free measurements (see Table 2 and compare the few gas free CO₂ values in parentheses with adjacent laboratory values). However, if the CO₂ values measured in the laboratory are multiplied by 2 to correct for the maximum pressure exposure of 2 ATA (reflecting the actual partial pressure exposure of divers), many of these samples exceeded the PEL for CO₂. To the best of our knowledge, all gas free testing was done by sampling the air at the entry each ballast tank before divers entered. This procedure may have produced lower CO₂ readings than those of our cylinder samples taken farther into the ballast tanks after divers have entered and removed their gear. However, the degree to which diverexpired CO₂ affects the ballast tank atmosphere is unclear, as most of our cylinder samples were collected at the beginning of the operation — a procedure that should have minimized any such effect, as would the relatively large gas volumes of the ballast tanks. Another possibility explaining the low gas free measurements of CO₂ compared to those of the cylinder samples is that purging of the sampling lines with ballast tank air may have been inadequate before gas free readings that resulted in air with lower CO2 in the lines were taken.

All CO samples were well below the 50 ppm PEL and, with the exception of those from one submarine (USS HAMPTON, with 6 ppm measured in the laboratory), were ≤1 ppm. The USS HAMPTON result agrees with the one gas free reading of 7 ppm reported above for this submarine in the **Gas free testing results** section.

In nearly all cases ballast tank air samples contained only low levels (up to several ppm each) of some VOCs, with estimated total VOC values of less than 10 ppm (excluding methane). The most commonly identified VOC other than methane (at levels up to 6 ppm, with the exceptions noted next for USS HAMPTON) was Freon 114, which was found in all samples at levels up to 4 ppm. However, the two sets of samples from the same ballast tank from USS HAMPTON that were taken in June and September 2002 contained considerably higher concentrations of VOCs than those from the other submarines: we estimated total VOCs from USS HAMPTON to be at levels up to ~50–150 ppm along with up to 25 ppm methane.

The VOCs from USS HAMPTON on both occasions consisted mainly of a complex mixture of aliphatic hydrocarbons containing from 6 to 14 or more carbon atoms. This

conclusion is based on MS library search results unverified by actual injections of these compounds. Some of these contaminants were estimated to be at levels up to 20 ppm each. There were also lower concentrations of a mixture of aromatics including toluene and xylenes. Samples from one of the USS ALBANY ballast tanks also contained an aliphatic profile similar to that of USS HAMPTON but at a total VOC level up to ~25 ppm. It is unknown whether these contaminants from the two submarines were from the air used for the LP blow or from within the ballast tank itself. However, the nature of the VOCs suggests that a petroleum-based external source such as fuel oil or diesel may have been contaminating the LP blow air. Whether some of the aromatic fraction is due to prior painting of any of the ballast tanks is unknown.

The VOCs from USS HAMPTON and USS ALBANY were not and should not be expected to be detected with current gas free procedures: the catalytic combustible gas sensors in the analyzers used for gas freeing are not designed to be trace gas analyzers and are generally unreliable for VOCs <200 ppm. The readout resolution of these instruments is frequently in 1% increments from 0 to 100% of the LEL, with the LEL for common gases such as hexane, propane, and methane ranging from 1 to 5% of the gas in air. Thus, the resolution of 1% roughly agrees with the lower limit of reliable detectability.

For comparison of exposure limits for some VOCs, octane has a threshold limit value—time-weighted average (TLV-TWA) of 300 ppm, and cyclohexane has a TLV-TWA of 100 ppm, as defined by the American Conference of Governmental Industrial Hygienists (ACGIH) for an eight-hour workday and 40-hour workweek. These are two of the compounds that may be present in the complex mixture from USS HAMPTON and USS ALBANY. At an estimated pressure inside the ballast tank of somewhat less than 2 ATA, the effective partial pressure exposure of this aliphatic mixture for USS HAMPTON might be estimated to be up to ~300 ppm. If the TLV-TWAs for all the aliphatic contaminants are assumed to be similar and the effects to be additive, the 150 ppm measured at 1 ATA but breathed at ~2 ATA might be of concern. This analysis ignores the aromatic component we detected in USS HAMPTON's samples. However, the question of potential health risk is increasingly complex and depends on other factors such as exposure times and physical activity rates.

CONCLUSIONS

1. The gas free procedures used at the two commands that we visited were similar and involved measuring O₂, CO₂, CO, combustible gas, and H₂S. However, the need to monitor combustible gas and H₂S is unclear, since the ballast tanks are ventilated daily with air from the LP blow system. Assuming that the daily ventilation meets the requirement of two times the estimated volume of the ballast tank, it is questionable how an explosive environment would be produced or how significant levels of H₂S would build up.

- 2. Our contaminant survey suggests the potential for large differences in the quality of the ballast tank air among submarines. For the six submarines, samples from only one, or possibly two, appear to warrant concern about VOCs. Carbon dioxide levels, when corrected for depth, exceeded gas free guidance in at least one sample from each of four submarines and were considerably higher than the gas free measurements. Although these findings are based on snapshots of the air quality at the time of our sampling and on a limited number of submarines, the air quality inside ballast tanks appears often to be outside acceptable ranges.
- 3. Although the degree to which divers' expired CO₂ affects the ballast tank atmosphere is unclear, the observed practices of not always performing gas free testing at hourly intervals during the diving operation and of not always testing for CO₂ are unjustified, in view of the elevated CO₂ levels observed in our samples. Such additional gas measurements taken as the diving operation is proceeding and taken well inside the ballast tank should more accurately represent the atmosphere to which divers are exposed.
- 4. In our opinion, instead of gas free screening with its ambiguity about what gases should be monitored, the emphasis for any air testing should be on ensuring a safe, breathable atmosphere inside the ballast tank during diving at pressures up to 2 ATA. The current failure to screen for VOCs, particularly in view of the elevated VOCs found on two submarines, puts diver safety at risk.
- 5. Using OSHA guidance for PELs to set limits for CO₂ and CO appears reasonable, although there is no apparent mechanism to update U.S. Navy procedures when OSHA substantially changes these PEL limits. In addition, there is no correction in either the CO₂ or CO limit for depth to reflect the twofold increase in partial pressure of contaminants to which divers might be exposed while working at levels greater than 1 ATA. Such a correction of exposure limits for pressure would agree with similar recommendations by the National Research Council, National Academy of Sciences for submarine atmospheres, ^{10,11} and would agree with current air screening procedures for the Dry Deck Shelter System. ¹² The acceptable O₂ range of 19.5 to 22.0% appears reasonable.
- 6. The limit for VOCs should be low enough to reduce the chances for unsafe exposures to expected contaminants but high enough to reduce chances of the limit being exceeded and thereby interfering with diving operations when there are no safety concerns. However, any "total contaminant" measurement such as that for VOCs will depend on the response factors of the specific VOC sensor(s) for the contaminants in the air as well as on the species used for quantification. Our contaminant survey begins to define the potential VOCs in ballast tank atmospheres.
- 7. The divers we met want to do, and should be doing, the air screening. The requirement to have a gas free qualified person on site to check the gas can delay the start of an operation by several hours and in our opinion does not ensure safe, breathable air inside the ballast tank.

- 8. The current procedure for sampling the ballast tank air with a pneumo hose seems acceptable and preferable to the other method also observed: that of using a length of Tygon tubing. To promote accurate sampling of VOCs, using soft plastic tubing such as Tygon, which can add or reduce VOCs from the gas, should be avoided. However, any gas sampling procedure should ensure adequate purging of the sampling line before measurements are taken, so that samples represent the ballast tank atmosphere. The use of plastic "sandwich bags" for sampling is reasonable in view of the relatively high gas flow rates that minimize any effect of the bag on the gas.
- 9. The personnel we met at the diving sites reported only rare incidents of either high gas (CO or CO₂) or low O₂ readings and of diver mishaps. How representative these anecdotal reports are among U.S. Navy ballast tank divers overall is unknown.
- 10. Following completion of this project, NEDU's Commanding Officer and personnel at several other diving commands not participating in this study held personal communications about ballast tank diving. Such communications indicated that, at one or more commands,
 - (1) Gas readings taken by the gas free engineer were corrected for depth by the on-site dive supervisor before comparisons were made to allowable limits.
 - (2) Gas free measurements were often taken continually during diving operations.
 - (3) When unacceptable gas readings were found, the ballast tank was sometimes ventilated.
 - (4) The recorded CO₂ readings commonly increased with the time divers were inside the ballast tanks and, when corrected for depth, were sometimes greater than the OSHA limit of 5000 ppm.

RECOMMENDATIONS

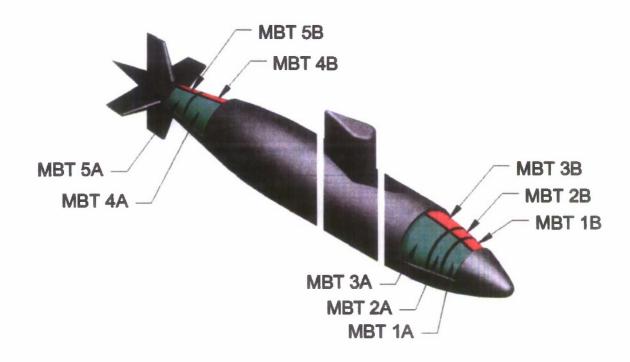
- 1. Before diving equipment is removed during ballast tank diving operations, the chemical safety of the ballast tank atmosphere should be evaluated in terms of O_2 , CO_2 , CO, and VOC levels. Divers performing the diving operation should be responsible for the air testing.
- 2. Current gas free procedures are inadequate for ensuring acceptable air exposures and should be eliminated, once improved procedures are established.
- 3. During ballast tank diving operations, the ballast tank atmosphere should continue to be monitored for O₂, CO₂, CO, and VOC levels on an hourly basis, as long as diving equipment remains removed.

- 4. Limits for CO₂ and CO should be based on OSHA guidance for PELs and a mechanism should be established to update U.S. Navy procedures when OSHA substantially changes these PEL limits. However, the current OSHA PELs for CO₂ and CO should be divided by a factor of 2 to correct for the maximum depth (2 ATA) to which ballast tank dives are conducted. The acceptable O₂ range of 19.5 to 22.0% should remain the same.
- 5. Revised air screening procedures for ballast tank atmospheres need to be developed, and these procedures should be based on the following guidance:
- a. <u>Screening instrument</u>. Although analyzers used for gas freeing are readily available from different vendors, currently no single monitor suitable for screening air for O₂, CO₂, CO, and VOCs is commercially available. Rather than use more than one instrument to analyze for O₂, CO₂, CO, and VOCs, we recommend that the air quality monitor now being developed by NEDU for U.S. Navy diving compressors be used, when approved for use, to screen ballast tank atmospheres. Thus, the same instrument will be used for multiple purposes.
- b. <u>VOC limit</u>. The VOC limit should be defined according to the sensitivity of the VOC detector of the compressor monitor to expected VOCs. Initially, assuming no additional air sampling is done from ballast tanks, we recommend that expected contaminants include both the broad range of aliphatic hydrocarbons that we observed from USS HAMPTON and USS ALBANY, and the common aromatic species, such as toluene and xylenes, that may well enter the LP blow system from dockside activities.
- c. <u>Procedures</u>. Procedures should include: (1) checks of equipment before use, (2) instrument calibration, (3) methods and hardware to allow sampling the ballast tank air topside, (4) action schedules based on exposure limits, (5) interpretation of results, (6) storage of instruments that are not in use, and (7) recommended or required routine maintenance of the testing gear. Emphasis should be on creating procedures that are simple to perform and that require minimal training. Included in the procedures should be steps to ensure that an LP blow of the ballast tanks has been performed just before entry, that sampling lines are adequately purged before gas measurements are taken, and that air samples are taken well inside the ballast tank where divers are working.
- d. <u>Field testing</u>. Draft air screening procedures that are developed need to be field-tested before they are approved and used to replace current gas free procedures.

REFERENCES

- 1. Naval Sea Systems Command, *U.S. Navy Diving Manual, Revision 5*, SS521-AG-PRO-010 (Arlington, VA: NAVSEA, 2005).
- 2. Naval Sea Systems Command, "Gas Free Engineering," in *Naval Ships' Technical Manual, Revision 3*, S9086-CH-STM-030 (Arlington, VA: NAVSEA, 1998), Ch. 074, Vol. 3.
- 3. Naval Sea Systems Command, *Gas Free Engineering Manual, Revision 01*, S6470-AA-SAF-010 (Arlington, VA: NAVSEA, 1999).
- 4. Newport News Shipbuilding, "Low-pressure Main Ballast Tank Blow System," in SSN688 Class Ship Systems Manual, S9SSN-W4-SSM-CC0(U) (Newport News, VA: Newport News Shipbuilding, 1998), Vol. 3, Pt. 1, Ch. 3.
- R. S. Lillo, A. Ruby, M. R. Bresnan, J. M. Caldwell, and D. W. Compton, Sampling of Breathable Air in U.S. Navy Sonar Domes, NMRI Technical Report No. 94-04, Naval Medical Research Institute, 1994.
- 6. R. S. Lillo and J. M. Caldwell, Laboratory Evaluation of the Analox Sub MK II P-S Prototype Hyperbaric O₂/CO₂ Analyzer, NEDU TR 05-16, Navy Experimental Diving Unit, Sept 2005.
- 7. Biosystems, Inc., Reference Manual PhD Ultra Multi Gas Detector (Middletown, CT: Biosystems, Inc., 1997).
- 8. National Institute for Occupational Safety and Health, *NIOSH Pocket Guide to Chemical Hazards* (Cincinnati, OH: U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, NIOSH, 2005).
- 9. American Conference of Governmental Industrial Hygienists, *Threshold Limit Values for Chemical Substances and Physical Agents* (Cincinnati, OH: American Conference of Governmental Industrial Hygienists, 2008).
- 10. National Research Council, *Submarine Air Quality* (Washington, DC: National Academy Press, 1988).
- 11. National Research Council, Review of Submarine Escape Action Levels for Selected Chemicals (Washington, DC: National Academy Press, 2002).
- 12. Naval Sea Systems Command, Dry Deck Shelter System, SSN 688 Class Host Ship Operating and Emergency Procedures, Revision 1, S9592-AP-MMM-A30 (Arlington, VA: NAVSEA, 2002), Vol. 3, Appendix L.

Figure 1. Main ballast tank (MBT) locations on an SSN 688 class submarine: green = starboard; red = port.



RIGHT-SIDE VIEW

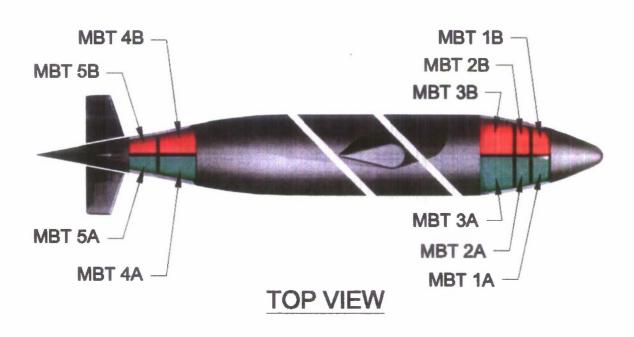


Table 1. Summary of Site Visits.

| SITE |
|-----------|
| |
| Norfolk |
| San Diego |
| Norfolk |
| |
| Norfolk |
| San Diego |
| |
| Norfolk |

*, A = starboard; B = port.

NV = Not visited; diving personnel took gas samples.

Table 2. Gas Analysis Results.

| SUBMARINE | SAMPLE DATE | BALLAST | 02 (%) | CO ₂ (ppm)* | (മർ) 00 |
|-------------------|-------------|------------|--------|------------------------|--------------|
| | | TANK | | Lab, (Gas Free) | |
| | 13 March 02 | 2B | 20.6 | 960-1815 | <1 |
| USS OKLAHOMA CITY | 14 March 02 | 3A | 20.5 | 1025-1485 | <1 |
| | 13 March 02 | 3B | 20.5 | 1130-1495 | <1 |
| | 4 April 02 | 3A | 20.5 | 680-1320 | <1 |
| | 4 April 02 | 3B | 20.4 | 545-760 | <1 |
| USS PORTSMOUTH | 26 March 02 | 44 | 20.3 | 1550-2315 | <1 |
| (2 visits) | 26 March 02 | 5 A | 20.6 | 610-1190 | <1 |
| | 17 April 03 | 2B | 19.5 | 2650-3305, (1500) | <1 |
| | 17 April 03 | 3A | 20.4 | 795-1075, (500) | ^1 |
| | April 03 | 4B | 19.7 | 1995-3545 | <1 |
| USS NEWPORT NEWS | 12 June 02 | 2B | 20.5 | 875-1520, (820) | <1 |
| USS HAMPTON | 13 June 02 | 5 A | 19.9 | 1950-2655, (720) | 9 |
| (2 visits) | .26 Sept 02 | 5 A | 20.3 | 1465-2745 | 1 |
| | 16 April 03 | 2A | 20.1 | 3495 | ^1 |
| USS HELENA | 16 April 03 | 2B | 19.8 | 2530-4695 | н |
| | 15 April 03 | 5B | 20.4 | 1810, (0) | <1 |
| | 15 April 03 | 2 A | 20.1 | 980-2020 | 1 |
| USS ALBANY | 15 April 03 | 2B | 20.0 | 2260-2770 | П |
| | 21 April 03 | 5 A | 20.4 | 1100-2835, (337) | <1 |

⁼ laboratory values and, when available, gas free measurements of ${\rm CO}_2$ in parentheses. Accuracy for analysis of O_2 and CO_2 is estimated at $\pm 1\%$ relative; accuracy for CO is

Results for VOCs are reported in the text of this report.

estimated at ±1 ppm.